

Free electron approximation for electron states of poly(*p*-phenylene vinylene) and other conjugated systems.

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(February 2, 2008, file ary4pfeo.tex)

Free electron approximation for electron states in poly(*p*-phenylene vinylene) and other conjugated systems is proposed. It provides simple and clear analytical expressions for energies of electron states and for wave functions. The results are in qualitative agreement with experiments. Our model does not contain fitting parameters. We present two examples of the developed theory applications: exact calculation of electron energy in magnetic field, and scattering of electrons in copolymer.

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I. INTRODUCTION

The valence effective Hamiltonian method is used for many years as a theoretical basis for band structure calculation of conjugated polymers, see Ref. 1 and literature cited therein. However, very simple approximate calculations can be performed in framework of introduced by Schmidt² free electron model, see more references in book of Salem³. This method is useful for classification of states of one-dimensional chain molecules and aromatic molecules. In the latter case it is known as Platt's Perimeter Model⁴ or Perimeter Free Electron Orbital Theory(PFEO)⁵. However, arylene based polymers, like poly(*p*-phenylene vinylene) (PPV) or poly(1,4-naphthalene vinylene) (PNV), are not purely one-dimensional, because they contain branching points. The generalization of free electron approach to this case is the main purpose of the present work. For the first time such calculations were undertaken by Ruedenberg and Scherr⁶ and here we develop the free electron network model starting with symmetry arguments.

We also would like to consider the basic question why there exists significant difference in characteristic energy scales of polyacetylene and PPV π -electron bands structure. The answer was given in the work of Soos *et al*.⁷. In the cited work authors addressed the small energy scale of the band structure of PPV to the presence of phenyl rings. The bands of PPV are formed from the levels of isolated phenyl ring (benzene molecule). The band width is determined by the coupling between the rings, which can be obtained by the canonical transformation from the coupling between adjacent carbon atoms.

In the present work we calculated the structure of PPV π -bands by means of constructing of π -states from free electron wave functions. In our model the proposed in Ref. 7 topological gap is the consequence of the time-

reversion symmetry of the wave function near the triple nodes. Triple node is carbon atom bound to three other carbons. Therefore, the structure of π -bands of PPV is determined by the phases, which are accumulated by the wave function having passed from one triple node to another. Polymer deformations become unimportant in this model. However, the proposed here model is suitable only for organic structures build from conjugated carbon chains. Other kinds of organic structures cannot be described by this model.

We obtained PPV π -electrons wave functions in simple analytical form and their symmetry properties are explicitly seen. Symmetry of all PPV states is essentially different from the symmetry of benzene molecule states, because spatial oscillations period of free electron wave function changes continuously with energy. One cannot say that this or that PPV electron state originate from specific benzene molecule state. For example, almost all direct light absorption processes between two highest occupied bands and two lowest empty bands are dipole allowed, that agree with observed experimentally^{8,9} four absorption bands.

Effect of magnetic field can be taken in to account exactly in framework of our model. In the same way one can explain magnetic susceptibility anisotropy of benzene molecule¹⁰. Magnetic field induces ring current in benzene molecule and this effect gives main contribution in magnetic susceptibility anisotropy. In PPV magnetic field also induces currents in phenyl rings, and they give main contribution into PPV diamagnetic susceptibility. It is different from the susceptibility of equivalent number of isolated phenyl rings, because magnetic field induced shifts of electron energies in PPV and benzene molecule are different.

In pure PPV one can distinguish occupied valence band and empty conductance band. In order to obtain certain

concentration of free carriers, holes in the valence band and electrons in conductance band, one can dope polymer with impurities or create structural defects. Our model can be used for calculation of electron and holes transmission probabilities through structural defect, if it is build from conjugated carbon chains. In this work we considered naphthalene molecule inserted in PPV instead of phenyl ring in order to see how strong it reflects carriers.

The accurate mathematical formulation of our model is done in next section. The PPV and PNV bands structure calculated too. Developed method application to the calculation of the diamagnetic susceptibility is given in Sec. III. An example of electron scattering on monomer of a different kind embedded into polymer, is considered in Sec. IV. In the same section we give the explicit form of PPV wave functions. The results are summarized in Sec. V.

II. ELECTRON STATES OF PPV AND PNV.

Perimeter Free Electron Orbital Theory(PFEO)⁵ is a good tool for description of benzene molecule π -electrons states. In this approximation the local potential of the atoms is ignored, and it's assumed that electrons can move freely around the molecule ring. The electron wave function for such state is $\psi = \exp(ikr)$, where r is coordinate along the circular ring, and k is the wave number. The periodic boundary condition results in $kL = 2\pi n$, where L is the perimeter of the ring that is approximately 8.3\AA . So this theory gives sequence of benzene π -electron levels

$$\mathcal{E} = \frac{(2\pi\hbar)^2}{mL^2} n^2, \quad n = 0, 1, 2, \dots \quad (1)$$

Since we have one π -electron per each carbon atom, these six electrons occupy two lowest energy levels(levels with $n \geq 1$ are twice degenerate).

The big surprise is that the results of the above model are in good agreement with experiment in spite of benzene molecule complex structure. For example, carbons create periodic potential $V(r)$ along benzene ring perimeter. The first order correction to the energy of n -th state due to the presence of this potential is given by its matrix element $\langle n|V|n \rangle$. This matrix element will be different from zero if the period of the potential is equal to multiplied by integer number half the wave length of n -th state wave function. The period of $V(r)$ is $L/3$ due to the alternation of the $C-C$ bonds lengths, and the matrix element $\langle n|V|n \rangle$ is not zero for the state with $n = 3, 6, \dots$, but other states don't feel this potential. Therefore, the application of Eq. (1) is justified for low energy states $n \leq 2$.

The main idea of this work is to extend the above approach to PPV, see Fig. 1, which can be considered as a sequence of benzene molecules connected via short chain

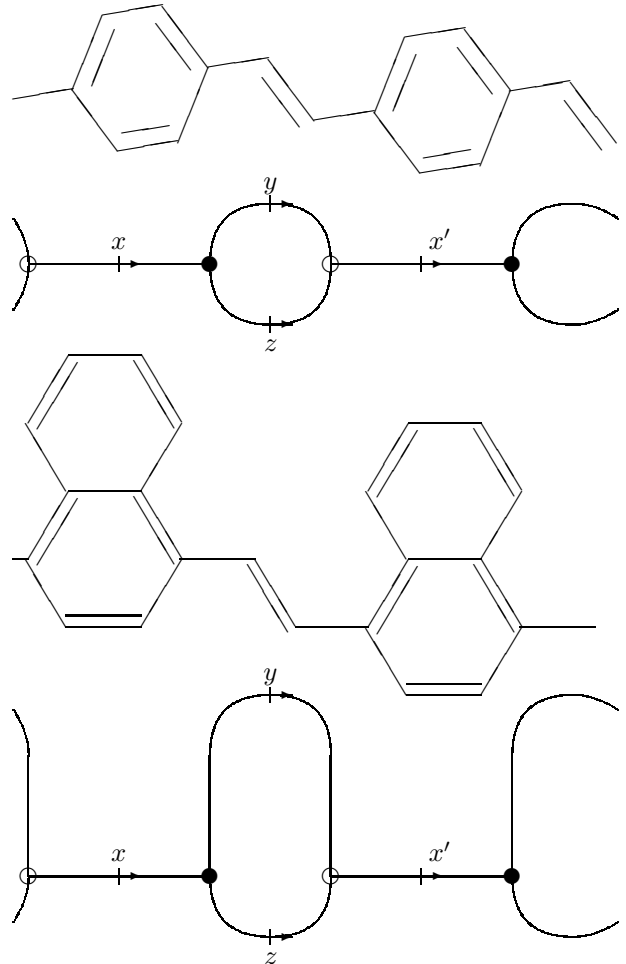


FIG. 1. Molecular structures of poly(*p*-phenylene vinylene) and poly(1,4-naphthalene vinylene). Schematic diagrams show choice of coordinates along carbon chains for our model. The short vertical lines mark the origins of corresponding coordinates.

of two additional carbons. In the framework of the considered model, electron runs along this short chain unless it reaches the phenyl ring. Here electron has some probability to come into the ring or to go back. The same picture repeats itself near the exit from the phenyl ring. We will obtain the valid state of PPV if electron wave function has the same amplitude after passing one monomer. Therefore, each unit cell of the polymer is modeled by the three bonds, as it is shown in Fig. 1, where the length of each bond is $L/2$. The electron can go from one bond to another at the nodes, which are marked by the open and filled circles in Fig. 1. The nodes correspond to carbon atoms bound to three other carbons.

Let's imagine the free electron wave is propagating along the bond. When the wave reaches the node the wave has amplitude r to be reflected and amplitude t to go to each remaining bond, see Fig. 2. The amplitudes to go left or right will be the same if we assume that the node has C_{3v} symmetry and the electron is in the ground state of the bond confinement potential. More rigorously, let's introduce coordinates x, y, z along three bonds attached to one node, black circle in Fig. 1, with origins at the middle of the corresponding bond. The electron wave functions in these bonds will be

$$\begin{aligned} Ae^{ikx} + Be^{-ikx}, \\ Ce^{iky} + De^{-iky}, \\ Ee^{ikz} + Fe^{-ikz}. \end{aligned} \quad (2)$$

Each wave leaving the node has to be linear combination of all the three waves coming in to this node,

$$\begin{aligned} Be^{-ikL/4} &= rAe^{ikL/4} + tDe^{ikL/4} + tFe^{ikL/4}, \\ Ce^{-ikL/4} &= rDe^{ikL/4} + tFe^{ikL/4} + tAe^{ikL/4}, \\ Ee^{-ikL/4} &= rFe^{ikL/4} + tAe^{ikL/4} + tDe^{ikL/4}, \end{aligned} \quad (3)$$

where phase $kL/4$ is acquired by electron having passed from the middle of the bond to the node.

The amplitudes t and r are complex numbers defined by the properties of the node. These amplitudes are not completely independent due to time reversion symmetry, see Fig. 2. The simple calculation results in two conditions

$$\begin{aligned} |r - t|^2 &= 1, \\ |r|^2 + 2|t|^2 &= 1. \end{aligned} \quad (4)$$

Therefore, two complex amplitudes t and r are defined by two real parameters, which can be chosen as following

$$\begin{aligned} t &= \sqrt{\frac{W}{2}} e^{-i\theta/2}, \\ r &= -\left(\sqrt{\frac{W}{8}} + i\sqrt{1 - \frac{9}{8}W}\right) e^{-i\theta/2}. \end{aligned} \quad (5)$$

Here $0 \leq W \leq 8/9$ and $0 \leq \theta < 2\pi$. The time reversion symmetry leads to some unusual property of "triple"

node transmission and reflection amplitudes. The absolute values of these amplitudes satisfy the conditions

$$0 \leq |t| \leq 2/3, \quad 1/3 \leq |r| \leq 1, \quad (6)$$

rather than the usual $0 \leq |r| \leq 1$, and $0 \leq |t| \leq 1$. Therefore, symmetric "triple" node always reflects electrons with the probability larger than $1/9$, and this is consequence of the time reversion symmetry.

Our purpose is now to find the states in PPV. Since the polymer is periodic structure, the electron wave function is characterized by quantum number ϕ . When electron pass one monomer, the wave function acquires this additional phase. Let say that considered previously two bonds, with coordinates y and z along them, join a new node, blank circle in Fig. 1, and make a loop. If the coordinate along third bond attached to this node is x' then the wave function in this bond will be

$$e^{i\phi} \left\{ Ae^{ikx'} + Be^{-ikx'} \right\}. \quad (7)$$

Application of the transmission and reflection rules to this node gives us three additional equations

$$\begin{aligned} Ae^{-ikL/4+i\phi} &= rBe^{ikL/4+i\phi} + tCe^{ikL/4} + tEe^{ikL/4}, \\ De^{-ikL/4} &= rCe^{ikL/4} + tEe^{ikL/4} + tBe^{ikL/4+i\phi}, \\ Fe^{-ikL/4} &= rEe^{ikL/4} + tBe^{ikL/4+i\phi} + tCe^{ikL/4}. \end{aligned} \quad (8)$$

Six equations, Eqs. (3,8), will be compatible if the matrix determinant of their coefficients is zero. This determinant has a following form, as a function of quantum number ϕ and energy, which is taken into account by phase factor $\exp(ikL)$,

$$\begin{aligned} Q &= \left[e^{-ikL} - (r - t)^2 \right] \left[(r + 2t)^2 (r - t)^2 \right. \\ &\quad \left. - \left(2r^2 + 2rt + t^2 + 4t^2 \cos(\phi) \right) e^{-ikL} + e^{-2ikL} \right]. \end{aligned} \quad (9)$$

The equation $Q = 0$ gives the dispersion relation for electron states in the polymer. It is a cubic equation for $\exp(ikL)$ and its three roots can be represented in the following form

$$\cos(kL - \theta) = (9/4)W - 1, \quad \sin(kL - \theta) > 0, \quad (10a)$$

$$\cos(kL - \theta) = W[5/4 + \cos(\phi)] - 1, \quad \sin(kL - \theta) > 0, \quad (10b)$$

$$\cos(kL - \theta) = W[5/4 + \cos(\phi)] - 1, \quad \sin(kL - \theta) < 0, \quad (10c)$$

where $k > 0$ due to our choice of the reflection and transmission events. The energies of the states are given by

$$\mathcal{E} = \frac{\hbar^2 k^2}{2m}, \quad (10d)$$

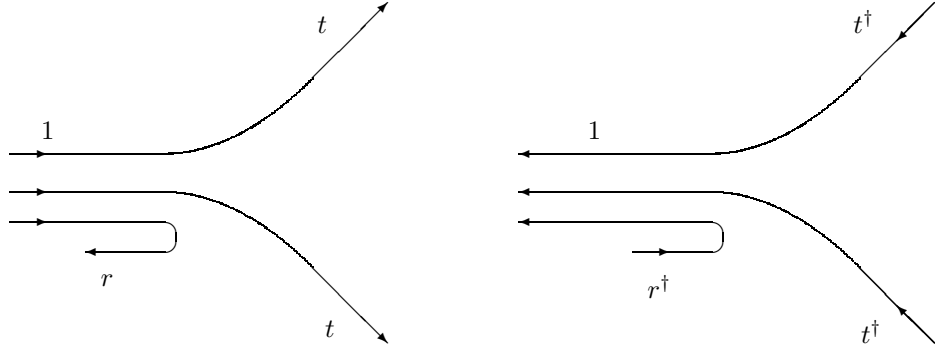


FIG. 2. The wave coming to the node has the reflection amplitude r , and transmission amplitude to go to each other branch t , see left figure. Inversion of time gives two conditions, see right figure. Amplitude of the wave going back has to be one and we obtain $1 = tt^\dagger + tt^\dagger + rr^\dagger$. Amplitudes of the waves passing to the branches has to be zero and therefore $0 = tr^\dagger + tt^\dagger + rt^\dagger$.

where m is a free electron mass.

Equation (10a) gives a sequence of isolated levels that corresponds to waves trapped in rings. One can easily verify that Eqs. (3,8) give for this case $A = B = 0$, and $C = -E$, $D = -F$. Equations (10b,10c) give a sequence of bands and envelop wave function is proportional to $e^{i\nu\phi}$, where ν is number of monomer in polymer chain. The amplitudes $A, B, C = E, D = F$ can be obtained from Eqs. (3,8), where k has to be considered as a function of ϕ given by Eq. (10b) or by Eq. (10c).

The comparison of the energy dispersions with numeric results of Ref. 1 shows that θ and W are energy independent and take the limit values: $\theta \approx 0$, $W \approx 8/9$. These numbers mean that electron does not acquire additional phase after passing triple node, and transmission of triple node is as good as it is allowed by time reversion symmetry. Therefore, θ and W take their limit values and should not be considered as fitting parameters. For these values¹¹ transmission and reflections amplitudes are real and $|t|$ takes its maximal value, $t = 2/3$, $r = -1/3$.

The energies of the isolated levels can be obtained from equation $\cos(kL) = 1$, and the dispersed band energies can be found from equation $\cos(kL) = [1 + 8 \cos(\phi)]/9$. The energies of six lowest bands, see Fig. 3, are given by Eq. (10d) and

$$\pi 1: kL = \arccos\left(\frac{1 + 8 \cos(\phi)}{9}\right), \quad (11a)$$

$$\pi 2: kL = 2\pi - \arccos\left(\frac{1 + 8 \cos(\phi)}{9}\right), \quad (11b)$$

$$\pi 3: kL = 2\pi, \quad (11c)$$

$$\pi 4: kL = 2\pi + \arccos\left(\frac{1 + 8 \cos(\phi)}{9}\right), \quad (11d)$$

$$\pi 5: kL = 4\pi - \arccos\left(\frac{1 + 8 \cos(\phi)}{9}\right), \quad (11e)$$

$$\pi 6: kL = 4\pi. \quad (11f)$$

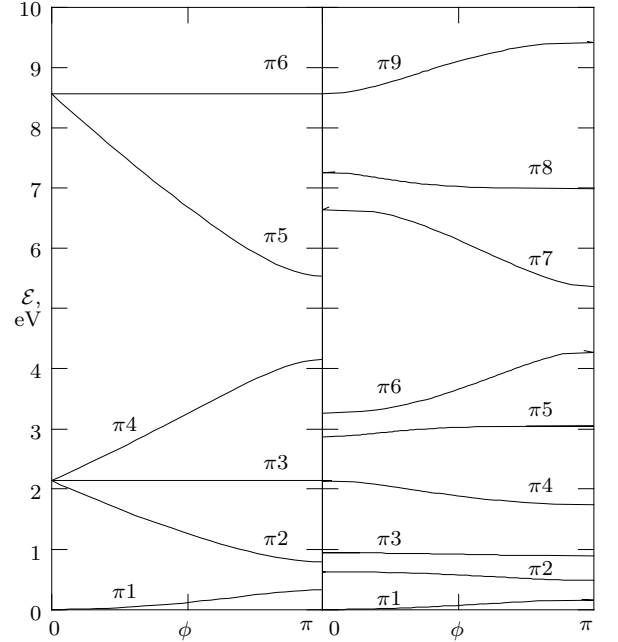


FIG. 3. The energies of calculated in the free electron approximation PPV and PNV π -bands. The only parameter in the calculations is perimeter of phenyl ring, $L = 8.3\text{\AA}$.

The bands $\pi 1 - \pi 4$ are occupied, and bands $\pi 5$ and $\pi 6$ are not. Really, we have 8 π -electrons per unit cell and they occupy four lowest bands. Fortunately, our model gives no states near $kL = 3\pi/2$, where the bands could be affected by the carbon chain periodic potential. However, the calculated energy gap between the top of the valence, $\pi 4$, band, where $kL = 3\pi - 2\arcsin(1/3)$, and the bottom of the conductance, $\pi 5$, band, where $kL = 3\pi - 2\arcsin(1/3)$, is still smaller than the experimentally measured value 2.4–2.5eV.

The symmetry of all obtained above states is essentially different from the benzene molecule states. It is because free electron wave vector k determines the coordinates dependence of the PPV wave functions and it changes continuously within the energy bands. The explicit form of the calculated from Eqs. (3,8) PPV wave function amplitudes are given in Sec. IV. One can immediately see that direct optical transitions $\pi 4 \rightarrow \pi 5$ and $\pi 3 \rightarrow \pi 6$ are dipole allowed⁷ and their dipole moment interband matrix element is parallel to PPV chain. Direct optical transitions $\pi 3 \rightarrow \pi 5$ and $\pi 4 \rightarrow \pi 6$ are dipole forbidden near the bands edges, $\phi = \pi$. The dipole moment interband matrix element increases rapidly with transition energy, and therefore, absorption bands corresponding to these processes also have to be experimentally observed. Our theory predicts following density of states peaks for four transitions: 1.4eV for $\pi 4 \rightarrow \pi 5$, 3.4 for $\pi 3 \rightarrow \pi 5$, 4.4 for $\pi 4 \rightarrow \pi 6$, and 6.4 for $\pi 3 \rightarrow \pi 6$. Three of these transition energies are in qualitative agreement with experimentally measured light absorption spectrum^{8,9}, which have features near 2.5eV, 3.7eV, 4.8eV, and 6.5eV.

The similar picture is observed in PNV. It is more sophisticated conjugated system synthesized recently.¹² The levels of naphthalene molecule are also well described by the PFEO model⁵. In other words π -electrons move freely around naphthalene molecule, see Fig. 1. In this model naphthalene molecule is replaced by two bonds, one of them having length $L/2$ and another having length $7L/6$. Equations similar to Eqs. (3,8) can be written for this model of PNV and from the condition of their compatibility we will obtain the following band structure:

$$\begin{aligned} \cos(\phi) = & \left\{ \frac{9}{8} \cos(2kL) + \frac{9}{8} \cos(5kL/3) + \frac{9}{8} \cos(4kL/3) \right. \\ & \left. + \frac{7}{8} \cos(kL) + \frac{7}{8} \cos(2kL/3) - \frac{1}{8} \cos(kL/3) \right\} \\ & / \left[\cos(kL) + \cos(2kL/3) + 2 \cos(kL/3) + 1 \right]. \end{aligned} \quad (12)$$

This is algebraic equation of order five for $e^{ikL/3}$. Its solution leads to sequence of bands, which are shown on Fig. 3. PNV has 12 carbon atoms in unit cell and six lowest bands are occupied. There are no states near $kL = 3\pi/2$ in this system, however the calculated energy gap between valence, $\pi 6$, and conductance, $\pi 7$, bands is still smaller than measured value¹² 2.3eV. The conductance band offset in possible PPV – PNV system is much

smaller than the gap, that is in agreement with experiment.

III. POLYMERS IN MAGNETIC FIELD.

Let's consider experiment in which polymers are prepared in a two dimensional layer. All the phenyl rings of the polymer will be also lying in the same plane. If one applies magnetic field perpendicular to that plane, electron propagating around phenyl ring will acquire the additional phase, Φ , which is equal to the magnetic flux via the ring divided by $\hbar c/e$. This additional phase can be easily introduced into Eqs. (3,8), and the determinant of the coefficients matrix becomes

$$\begin{aligned} Q = & \left\{ e^{-ikL} - (r-t)^2 \right\} \left\{ (r+2t)^2(r-t)^2 \right. \\ & - \left[2r^2 + 2rt - t^2 + 2t^2 \cos(\Phi) \right. \\ & \left. \left. + 4t^2 \cos(\phi) \cos(\Phi/2) \right] e^{-ikL} + e^{-2ikL} \right\}. \end{aligned} \quad (13)$$

Again the equation $Q = 0$ gives the dispersion relation for the electron states in the polymer. The states $\pi 3$ and $\pi 6$ are not affected by the magnetic field, this can be explained by the properties of these states. In such a state electron is not only localized in the phenyl ring, it is localized in one of the parts of the ring¹. Therefore electron in such a state does not go around the phenyl ring and does not know about the magnetic field.

The electron energy in other π -states is periodic function of magnetic flux

$$\mathcal{E}_{1,2}(\phi, \Phi) = \frac{\hbar^2}{2mL^2} \left[\pi \mp \gamma(\phi, \Phi) \right]^2, \quad (14)$$

$$\mathcal{E}_{4,5}(\phi, \Phi) = \frac{\hbar^2}{2mL^2} \left[3\pi \mp \gamma(\phi, \Phi) \right]^2, \quad (15)$$

$$\begin{aligned} \cos[\gamma(\phi, \Phi)] = & \frac{1}{3} - \frac{4}{9} \cos(\Phi) \\ & - \frac{8}{9} \cos(\phi) \cos(\Phi/2). \end{aligned} \quad (16)$$

Here $\gamma(\phi, \Phi) > 0$. The energy of $\pi 2$ and $\pi 5$ states decreases in weak magnetic field (paramagnetic states) and the energy of $\pi 1$ and $\pi 4$ states increases (diamagnetic states). For example, the energy gap between the conduction and the valence bands decreases with magnetic field, but the change is very small, since the area of the ring is very small, see Ref. 10, Eq. 4-37.

The above model does not take into account the curvature of the polymers. If the polymer has the points of the self crossing the electron states can get additional magnetic moment that depends on the tunneling probabilities at such points. The magnetic moment of π -states without considering of this effect can be obtained from

the derivatives of the energies with respect to magnetic field.

The total magnetic moment of the polymer is given by the summation of the magnetic moments of all the occupied states. The diamagnetic susceptibility of the layered polymer material at zero temperature can be obtained as a second derivative of the total energy of the system with respect to magnetic field. The approximate expression for the susceptibility per delocalized electron is

$$\chi = N \int_{-\pi}^{\pi} \frac{d\phi}{2\pi} \left(\frac{Se}{\hbar c} \right)^2 \frac{\partial^2}{\partial \Phi^2} \left\{ \frac{\mathcal{E}_2(\phi, \Phi) + \mathcal{E}_4(\phi, \Phi)}{2} \right\}, \quad (17)$$

where S is phenyl ring area and N is number of monomers. In this expression we average susceptibility over delocalized states in the energy interval corresponding to $\pi < kL < 3\pi$. One can check that the averaged susceptibility in interval $0 < kL < \pi$ is the same. It is convenient to express χ in terms of obtained from PFEOT theory benzene molecule susceptibility per electron¹³, $\chi_0 = S^2 e^2 / (mc^2 L^2)$. Numeric integration with respect to ϕ gives $\chi \approx 0.7N\chi_0$. Since PPV has six delocalized π electrons per monomer, the PPV magnetic susceptibility per mole of monomers has to be equal 0.7 of benzene molecule molar diamagnetic susceptibility:

$$\chi_{\text{PPV}} = 0.7\chi_{\text{C}_6\text{H}_6} \quad (18)$$

IV. SCATTERING OF FREE ELECTRON WAVES IN COPOLYMER.

The last example for the application of our almost heuristic theory to the real physical problems is consideration of what will happen if we replace one monomer in a polymer by monomer of a different kind. Let's consider the copoly(*p*-phenylene vinylene – 1,4-naphthalene vinylene), which was used in recent experiments¹⁴. This system can be obtained formally from PPV if one replaces part of phenyl rings by naphthalene molecules. If the naphthalene concentration is small, we can consider each monomer of 1,4-naphthalene vinylene as an impurity or a structural defect in PPV chain. Therefore, such monomer partially reflects electrons propagating in PPV bands.

We start the calculation of naphthalene vinylene monomer transmission coefficient with derivation of pure PPV wave functions. Three quantum numbers n , κ , and $s \equiv \text{sign}(\gamma)$ specify each PPV π electron state, see Eq. (19) below. Therefore, the wave functions of all PPV π states are given by the amplitudes $A = A_0(n, s, \kappa)$, $B = B_0(n, s, \kappa)$, $C = C_0(n, s, \kappa)$, $D = D_0(n, s, \kappa)$, $E = E_0(n, s, \kappa)$, $F = F_0(n, s, \kappa)$, which can be calculated for given energy from Eqs. (3,8). Their explicit forms are

$$A_0 = \frac{1}{\sqrt{2L|\cosh(\xi)|}} e^{\xi/2}, \quad (19a)$$

$$B_0 = \frac{1}{\sqrt{2L|\cosh(\xi)|}} e^{-\xi/2}, \quad (19b)$$

$$C_0 = E_0 = \frac{i}{\sqrt{4L|\cosh(\xi)|}} e^{i\kappa/2 + \xi/2}, \quad (19c)$$

$$D_0 = F_0 = -\frac{i}{\sqrt{4L|\cosh(\xi)|}} e^{i\kappa/2 - \xi/2}, \quad (19d)$$

$$\cosh(\xi) = 3 \sin(\gamma/2), \quad (19e)$$

$$\sinh(\xi) = 2\sqrt{2} \sin(\kappa/2), \quad (19f)$$

$$\cos(\gamma/2) = \frac{2\sqrt{2}}{3} \cos(\kappa/2) \quad (19g)$$

$$\phi = \begin{cases} \pi + \kappa, & \phi > 0, \quad \kappa < 0, \\ -\pi + \kappa, & \phi < 0, \quad \kappa > 0, \end{cases} \quad (19h)$$

$$k_0 L = (2n + 1)\pi + \gamma, \quad -\pi \leq \gamma \leq \pi \quad (19i)$$

where the wave function is normalized on one particle per unit cell of the polymer. In this system of equations free electron wave vector is also the function of quantum numbers $k = k_0(n, s, \kappa)$. Vice versa, k determines the quantities κ, γ, ξ, n , and thus all of them are functions of energy. Dimensionless wave number κ is more convenient than ϕ , which was used in Eqs. (11) and Fig. 3, because κ goes to zero near the top of valence band and near the bottom of conductance band. There are two states for each pair of quantum numbers n and κ , one state with positive γ , $s = 1$, and one state with negative γ , $s = -1$. For example the states in the conductance and valence bands are given by $n = 1$, with $s = \pm 1$ correspondingly. One can verify that the bands are parabolic near the edges, where $|\kappa| \ll 1$.

Equation 19g is not necessary, but introduced for convenience. When γ is negative, the quantity ξ has imaginary part, which is equal to $i\pi$. Since dimensionless wave number κ have to be real Eq. 19g gives $\cos^2(\gamma/2) \leq 8/9$. Therefore, the allowed values of γ lie in the intervals $-\pi \leq \gamma \leq -\gamma_0$ and $\gamma_0 \leq \gamma \leq \pi$, where $\gamma_0 = 2 \arcsin(1/3)$. The state is carrying electron, and flux is

$$j = \frac{\hbar k}{mL} \tanh(\xi), \quad (20)$$

which show the physical meaning of ξ .

Embedding of naphthalene vinylene monomer in to PPV chain result in scattering of electrons and holes with dimensionless wave number κ . In order to calculate transmission, T , and reflection, R , coefficients we have to write equations similar to Eqs. (3,8) for PNV free electron model, see Fig. 1, and substitute

$$\begin{aligned} k &= k_0(n, s, \kappa), \\ A &= A_0(n, s, \kappa) + R A_0(n, s, -\kappa), \\ A' &= T B_0(n, s, \kappa), \\ B' &= T B_0(n, s, \kappa). \end{aligned}$$

$$\begin{aligned} B &= B_0(n, s, \kappa) + RB_0(n, s, -\kappa) , \\ B' &= TB_0(n, s, \kappa) . \end{aligned} \quad (21)$$

Here one have to use $n = 1$ and $s = \pm 1$ for conduction and valence band correspondingly. The further calculations are straightforward, the qualitative results are the following. Near both conduction and valence bands edges transmission probability $|T|^2 \approx 0.8\kappa^2$, and therefore it is proportional to the kinetic energy of quasiparticles. Far from the edges it becomes of the order of one.

V. SUMMARY.

We have developed a new free electron model of PPV, which allows to calculate band structure of polymer and hold wave functions of π electrons in simple analytical form. We showed that the band structure contains only one parameter, which is the averaged distance between two neighboring carbons. The symmetry of PPV wave function allows direct optical transitions from $\pi 3$ and $\pi 4$ states to $\pi 5$ and $\pi 6$ states, that explain four bands observed on absorption spectrum. The calculated energy gap between $\pi 4$ and $\pi 5$ states is not in agreement with experiment, but energies of three other transitions are in agreement. This supports importance of many-body polaronic¹⁵ and excitonic^{16,17} effects for transitions near the energy gap. Similar models can be developed for other conjugated systems, for graphite planes or more complicated polymers.

We have calculated exactly the magnetic field dependence of electron energies, which is due to presence of phenyl rings. The diamagnetic susceptibility per monomer of PPV have been found approximately to be 0.7 of the susceptibility anisotropy of isolated benzene molecule. We also considered scattering of electrons on polymer structural defects. We found that PPV electrons and holes transmission probability through 1,4-naphthalene vinylene monomer inserted in polymer is proportional to their kinetic energy. This is according to general property of scattering on potential occupying final volume of space. We believe that proposed model have many potential applications.

ACKNOWLEDGMENTS

We wish to acknowledge prof. Dan Davydov whose talk about conjugated polymers initiated this work, prof. Boris Laikhtman for discussion of this work and criticism of the manuscript, and Slava Rotkin for discussion of the results.

- ¹ M. Lögdlund, W. R. Salaneck, F. Meyers, J. L. Brédas, G. A. Arbruckle, R. H. Friend, A. B. Holmes, G. Froyer, *Macromolecules* **26**, 3815 (1993).
- ² O. Schmidt, *Ber. Deut. Chem. Ges.* **73A**, 97 (1940).
- ³ L. Salem, *The molecular orbital theory of conjugated systems*. (W. A. Benjamin, INC., New York, 1966), Chap. 7. Molecular orbital theory and the excited states of conjugated systems. UV Spectra.
- ⁴ J. R. Platt, *J. Chem. Phys.* **17**, 484 (1949).
- ⁵ M. Pope and C. E. Swenberg, *Electronic properties in organic crystals* (Oxford University Press, New York, 1982), Chap. I.B. Molecular excited states., p. 7.
- ⁶ K. Ruedenberg and C. W. Scherr, *J. Chem. Phys.* **21**, 1565(1953)
- ⁷ Z. G. Soos, S. Etemad, D. S. Galvão and S. Ramasesha, *Chem. Phys. Lett.* **194**, 341 (1992).
- ⁸ D. A. Halliday, P. L. Burn, R. H. Friend, D. D. C. Bradley, A. B. Holmes, and A. Kraft, *Synth. Met.* **55-57**, 954 (1993).
- ⁹ J. Cornil, D. Beljonne, R. H. Friend, J. L. Brédas, *Chem. Phys. Lett.* **223**, 82 (1994).
- ¹⁰ L. Salem, *The molecular orbital theory of conjugated systems*. (W. A. Benjamin, INC., New York, 1966), Chap. 4. Molecular orbital theory of the Magnetic Properties of closed Shells.
- ¹¹ We also made a calculation of a dispersion law of π -electrons of graphite planes and found from the fitting of our result to other data $\theta \approx 0$ and $W \approx 7.75/9$.
- ¹² M. Onoda, M. Uchida, Y. Ohmori, K. Yoshino, *Jpn. J. Appl. Phys.* **23**, 3895 (1993).
- ¹³ L. Pauling, *J. Chem. Phys.* **4**, 673 (1936).
- ¹⁴ H. Hong, D. Davidov, E. Farage, H. Chayet, R. Neumann, and Y. Avny, , privet communication.
- ¹⁵ Y. Furukawa, *Synth. Met.* **69**, 629 (1995).
- ¹⁶ M. Chandross, S. Mazumdar, S. Jeglinski, X. Wey, Z. V. Vardeny, E. W. Kwock, and T. M. Miller, *Phys. Rev. B* **50**, 14702 (1994).
- ¹⁷ Yu. N. Garstein, M. J. Rice, and E. M. Conwell, *Phys. Rev. B* **52**, 1683 (1995).